AD-A011 688

THE INFLUENCE OF MICROSTRUCTURE ON FRACTURE OF
CERAMICS

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Prepared for:

Air Force Office of Scientific Research

14 May 1975

195040

AFOSR - TR - 75 - 0 8 2 1

Final Technical Report

(11/1/73 to 4/30/75)

ADA011688

THE INFLUENCE OF MICROSTRUCTURE ON FRACTURE OF CERAMICS

AFOSR GRANT #74-2603

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JUN 20 1975

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DATE: May 14, 1975

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR - TR - 75 - 0 8 2 Γ	2 GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) THE INFLUENCE OF MICROSTRUCTURE ON FRACTURE OF CERAMICS		5. TYPE OF REPORT & PERIOD COVERED Final
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) C. Norman Ahlquist Rishi Raj		8. CONTRACT OR GRANT NUMBER(s) AFOSR-74-2603
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Mechanical Engineering University of Colorado Boulder, Colorado 80302		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 9761-01 61102F
11. CONTROLLING OFFICE NAME AND ADDRESS AFOSR/NE 1400 Wilson Blvd. Arlington, VA 22209		12. REPORT DATE 14 May 75
		13. NUMBER OF PAGES 19
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCL/UNCL
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release, distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A technique has been developed for the measurement of the viscosity of the amorphous phase in the grain boundaries of silicon nitride. The technique will serve as a useful tool in the development of these ceramics since a correlation can now be established between the viscosity of the grain-boundary phase and its chemistry. Two grades of commercial silicon-nitride have been tested -- HS110 and HS130 and have a measured viscosity of about 5×10^{15} Poise/cm per unit thickness of the grain-boundary phase at a temperature of about 900°C. Some work has also been completed on building models for intergranular fracture in

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these materials based upon the concept of fracture in a thin viscous adhesive layer sandwiched between two hard surfaces. A simple model which considers fracture by the growth of penny-shaped voids in the adhesive layer gives sensible agreement with actual fracture measurements in silicon-nitride at elevated temperatures. The relationship between yielding and fracture in semi-brittle ceramic crystals has also been investigated. Strengthening of I-VII compounds, e.g. KCl, NaCl, and LiF, by divalent impurity additions is accompanied by an increase in fracture energy. The observed increase is explained as a result of microcrack nucleation at intersection slip bands.

1. ABSTRACT

This report is in two parts which cover consecutive Periods I and II of the duration of the grant.

      PERIOD I : Nov. 11, 1973 to July 31, 1974

      PERIOD II: Aug. 1, 1974 to April 30, 1975

The reason for this division is that during Period I the work concentrated upon fracture in semi-brittle ceramic crystals at low temperature and during Period II fracture in hot-pressed ceramics at elevated temperature was emphasized.

PERIOD I

The relationship between yielding and fracture in semi-brittle ceramic crystals has been investigated. Strengthening of I-VII compounds, e.g. KCl, $NaCl$, and LiF, by divalent impurity additions is accompanied by an increase in fracture energy. The observed increase is explained as a result of microcrack nucleation at intersecting slip bands.

The interaction of cleavage cracks with dispersed hard and soft second phase particles was observed using optical microscopy. The dispersed particles generate cleavage steps which increase the fracture energy by approximately a factor of two.

The solution strengthening of MgO by dissolved transition metal cations is examined. Trivalent cations harden MgO equally while divalent cations have little effect upon yield strength. The observed hardening is quantitatively explained as a result of the change in electrostatic energy that occurs when a trivalent ion pair - cation vacancy complex is sheared by a dislocation passing through the complex.

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PERIOD II

Hot-pressed ceramics such as silicon-nitride are promising candidates for the next generation of structural materials for application at elevated temperature. The limiting factor in the high temperature strength (resistance to creep and to fracture) of these materials is the presence of a 100 - 1000A° thick amorphous phase in the grain boundaries which flows viscously at elevated temperature. We have successfully developed a technique for the measurement of the viscosity of this phase. The technique can serve as a useful tool in the development of these ceramics since a correlation can now be established between the viscosity of the grain-boundary phase and its chemistry. We have tested two grades of commercial silicon-nitride -- HS110 and HS130 (Norton Company) -- and have measured a viscosity of about 5×10^{15} Poise cm^{-1} per unit thickness of the grain-boundary phase at a temperature of about 900°C.

Some work has also been completed on building models for intergranular fracture in these materials based upon the concept of fracture in a thin viscous adhesive layer sandwiched between two hard surfaces. A simple model which considers fracture by the growth of penny-shaped voids in the adhesive layer gives sensible agreement with actual fracture measurements in silicon-nitride at elevated temperatures.

2. PROGRESS REPORT

PERIOD I

Three publications resulted from the work during this period. This level of productivity was the direct result of the continuity of effort provided by a previous AFOSR Grant #72-2172. The important results from each of these publications are described below.

Publication I

Influence of Yield Strength on Fracture of Semi-Brittle Ceramic Crystals

The range of use of alkali halide crystals in weight critical laser window applications can be extended if the yield strength of these crystals were increased without degrading their optical properties. One method of strengthening without severe increases in optical absorption is by solid solution hardening. In these semi-brittle crystals, crystals with high dislocation mobility but less than 5 independent slip systems, the occurrence of plastic deformation has a strong influence on crack formation. The purpose of the following research (1)[*] was to investigate the relationship between yield strength and toughness (meaning specifically the apparent fracture surface energy, γ_i) in semi-brittle ceramic crystals whose strength was varied through the controlled addition of divalent impurities.

The apparent fracture surface energy was measured using the double cantilever beam technique for a series of LiF single crystals doped with Mg^{++} or Ca^{++}. These divalent cations strongly harden alkali halide crystals. Contrary to the usual metallic behavior where an increase in strength is accompanied by a decrease in toughness, in LiF increasing the yield strength by a factor of 4 was accompanied by a 50-100% increase in γ_i, Fig. 1.

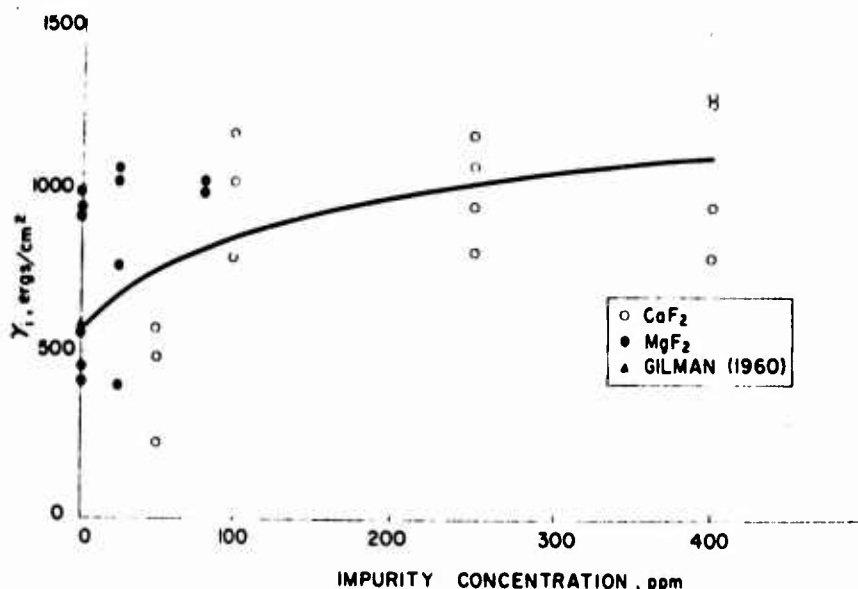[*] ( ) references listed under publications.

Fig. 1. Apparent Surface Energy for Fracture Reinitiation, γ_i , vs. Divalent
Impurity Concentration (Proportional to Yield Strength Squared).

The mechanism responsible for the measured increase in γ_i with
increasing yield strength was attributed to the classic Cottrell-Stroh
microcrack nucleation mechanism at intersecting slip bands. This
mechanism was originally developed for fracture of bcc metals but is
equally applicable to fracture of semi-brittle ceramics whose $\{110\}$ $<110>$
slip systems intersect certain $\{100\}$ cleavage planes at the optimum
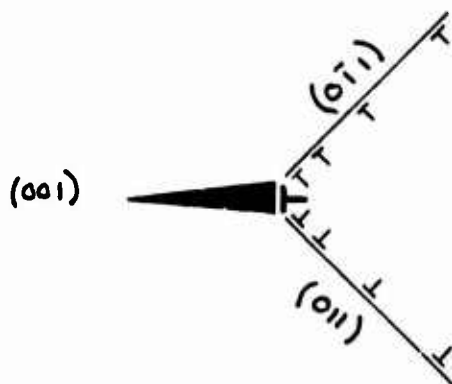Schmid orientation of 45°, Fig. 2.

Fig. 2. Coalescence of Two $\{110\}$ $<110>$ Slip Bands to Form a $\{100\}$
Cleavage Knife.

Publication II

The Interaction of Cleavage Cracks with Second Phase Particles

The application of ceramics at elevated temperatures can be limited by the materials capacity to resist fracture due to thermal shock. Thus, the development of tough microstructures which maintain their integrity at high temperatures is of practical interest. One potential method of improving both strength and toughness is by dispersion or precipitation of second phase particles. In the research described herein, the direct observation of the interaction of running cleavage cracks with second phase particles lying on or near to the fracture surface is reported (2). Lithium flouride and magnesium oxide were chosen as the matrix for these experiments because (i) they are transparent; (ii) single crystals can be grown containing hard particles (CaF_2 in LiF) or soft particles (voids in MgO), and; (iii) LiF and MgO cleave.

Single crystals were prepared containing dispersions of <u>hard</u> or <u>soft</u> second phase particles. Double cantilever beam samples were cleaved at room temperature. The cleaved halves were examined optically to observe the second phase particle - cleavage crack interaction. Cleavage steps on the fracture surface always lie parallel to the direction of crack propagation and provide a method of plotting consecutive positions of the crack front.

Figure 3 shows three <u>hard</u> CaF_2 particles lying on the {100} fracture surface. The direction of crack propagation is from left to right as indicated by the arrow. Consecutive positions of the crack front are plotted as dotted lines. Notice that a large cleavage step forms on the back side of each particle whose height increases with particle diameter--compare the two large particles in the center of the micrograph to the small particle just beneath the arrow.

100 μ

Fig. 3. Cleavage Step Pattern Around Hard CaF$_2$ Particles in LiF Crystal.

An example of cleavage steps formed at soft particles (cubical voids) is shown in Fig. 4.
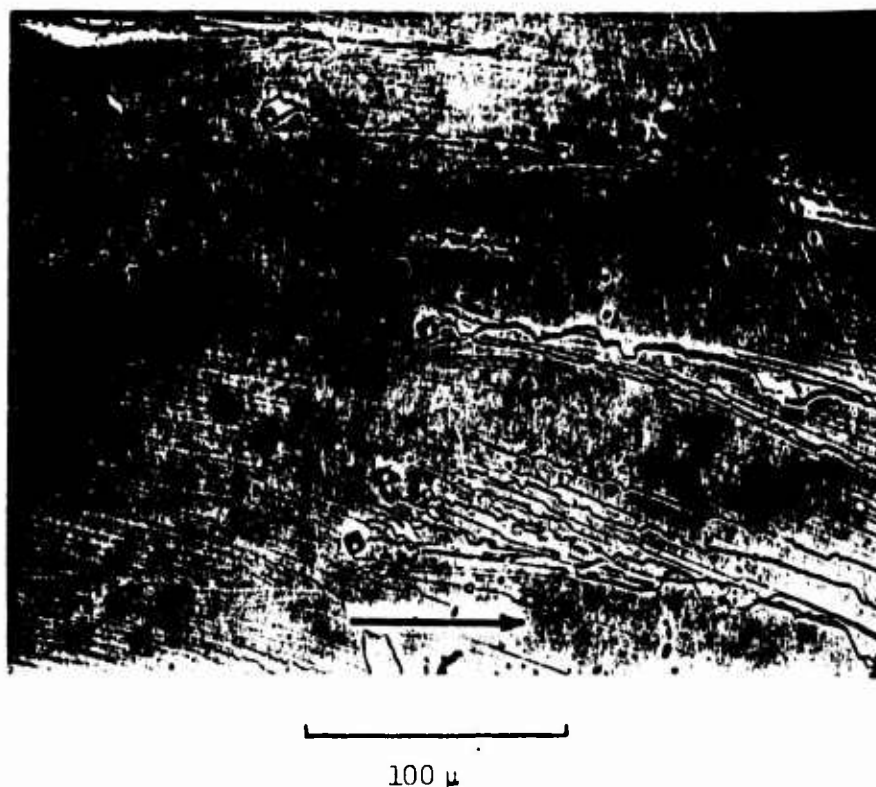
100 μ

Fig. 4. Cleavage Steps Nucleated at <u>Soft</u> Cubical Voids in MgO Crystal.

This micrograph was taken near the site of crack extension. The apparent fracture surface energies for void free crystals and crystals containing the preceding void distribution were 1800 and 3600 ergs/cm^2, respectively. The observed increase in γ_i is consistent with the additional work done in forming the observed cleavage steps by shearing at a stress equal to the theoretical shear strength.

Publication III

Solution Strengthening of MgO Crystals

The mechanism responsible for the intense hardening of alkali-halide crystals by divalent cations and of MgO by trivalent cations was examined (3). Single crystals of MgO were obtained containing controlled additions of Al^{3+}, Cr^{3+} and Fe^{3+}. Their yield strength was measured and correlated with the impurity concentration. The yield strength, σ_y, was found to follow a relation of the form:

$$\sigma_y = \sigma_o + B \, c^{1/2},$$

where $\sigma_o = 0.7 \times 10^9$ dynes/cm^2, $B = 33 \times 10^9$ dynes/cm^2 and c is the total trivalent impurity concentration. Further, all data fall on a common line independent of the particular trivalent cation as shown in Fig. 5. This behavior is inconsistent with elastic theory for pinning of dislocations at tetragonal defects.
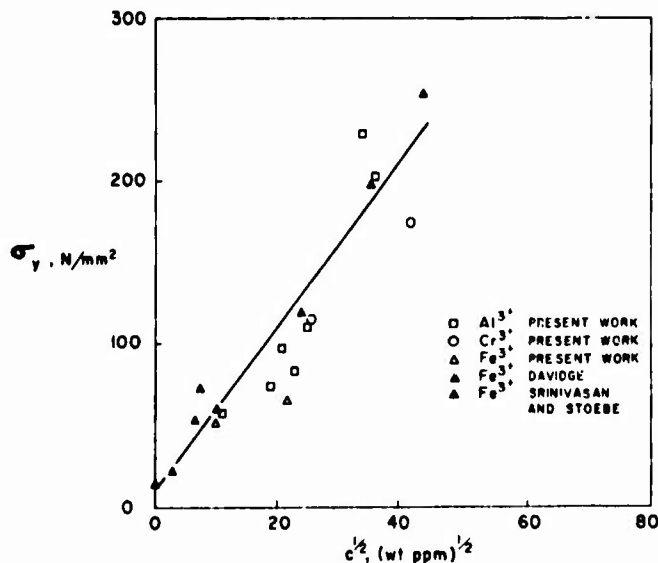

Fig. 5. Dependence of Yield Strength on Square Root of Trivalent Cation Concentration for MgO Crystals.

The solution hardening by Al^{3+}, Cr^{3+} and Fe^{3+} is quantitatively explained by a recent theory due to Gilman. Strengthening in this theory results from the change in electrostatic energy that occurs when a trivalent ion pair - cation vacancy complex is sheared by a dislocation passing through the complex, Fig. 6.
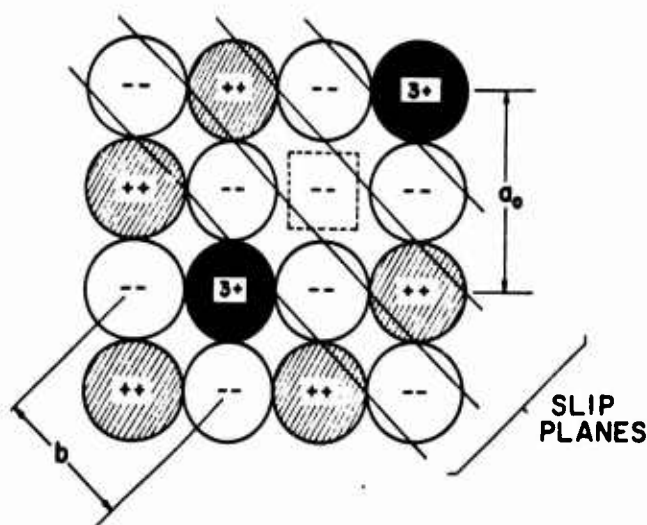
Fig. 6. Trivalent Ion Pair - Cation Vacancy Complex Shown Schematically on the {100} Plane of the MgO Structure.

The hardening coefficient B in this model is equal to:

$$ B = 4.7 \left(\frac{z^2 e^2}{K a_o^4} \right) \quad , $$

where z is the effective charge on the trivalent impurity, e is the electronic charge, K is the static dielectric constant and a_o is the lattice parameter. This model predicts that the hardening should be independent of the particular trivalent impurity as it only depends upon the effective charge on the impurity and K and a_o of MgO.

The static dielectric constant and lattice parameter for MgO are K = 10.1 and a_o = 4.203 Å, respectively, yielding a numerical value for B of

$$ B = 34 \times 10^9 \text{ dynes/cm}^2 \quad . $$

This compares favorably with the experimental value of

$$B_{exp} = 50 \times 10^9 \text{ dynes/cm}^2 .$$

This simple theory describes quantitatively the solution hardening of MgO by trivalent impurities. The predicted hardening coefficient, B, given by the theory differs from the observed value by 32% lending credence to the model.

PERIOD II

The work during this period concentrated upon a study of fracture in hot-pressed ceramics such as silicon-nitride at elevated temperature. Two papers resulting from this work have been submitted for publication; the first deals with the measurement of viscosity of the grain boundary phase in hot-pressed ceramics and the second presents a model for intergranular fracture by the growth of penny-shaped voids in the grain-boundary layer.

Publication IV

Measurement of Viscosity of the Grain-Boundary Phase in Hot Pressed Silicon-Nitride

A technique has been developed to measure the viscosity of the grain boundary phase in hot-pressed ceramics. It derives from the experiments performed by Kê (Phys. Rev. 71, 1947, p. 533) where he showed in an internal-friction experiment with metal that the presence of grain-boundaries leads to a damping peak. We have demonstrated by experiments with polycrystalline hot-pressed silicon-nitride that a similar peak is observed when the microstructure of the ceramic consists of hard grains held together by an amorphous grain boundary phase which flows viscously at elevated temperature. By using the results of an analytical model, the validity of which was proven in an earlier work (Mosher and Raj, Acta Met. 22, 1974, p. 1469), the results from the internal-friction experiments can be translated into a measure of the viscosity of the

grain boundary phase. Two grades of silicon nitride were tested -- HS110 and HS130 (Norton Company). The viscosity was found to be about 5×10^{15} poise cm^{-1} per unit thickness of the grain-boundary layer at a temperature of about 900°C. The viscosity of HS130 was approximately one order of magnitude greater than for HS110; this correlates well with the better high temperature mechanical properties (resistance to creep and to rate of intergranular crack growth) demonstrated by HS130. This technique can be used in the development of a hot-pressed ceramic which contains a high viscosity grain boundary phase; this ceramic can also be expected to have superior high temperature strength.

Publication V

De-Adhesion by the Growth of Penny Shaped Voids in an Adhesive Layer

This paper is an attempt to build models which explain the high temperature intergranular fracture behavior of hot-pressed ceramics The thesis is that voids can nucleate in the grain boundaries at inclusions, triple points or aa pre-existing holes left behind by an incomplete sintering process. When a tensile stress is applied across the boundary the voids grow in the grain boundary layer in the same manner as voids will grow in a thin adhesive layer confined between two parallel rigid plates. The voids, then, grow in the shape of a penny and eventually coalesce and cause fracture. This paper presents a rigorous analysis which correlates the rate of growth of the voids to the rate of separation of the boundary, to the applied normal traction, to the pressure within the voids, to the surface tension forces, and to the spacing of the voids in the boundary. The voids were assumed to be arranged in a periodic two-dimensional lattice in the grain boundary. The results of the analysis are shown to be true by simple experiments with a viscous oil.

The time-to-fracture at a constant applied stress was calculated. It is shown to vary inversely with the flaw density (number of bubbles per unit area) and inversely with the grain-boundary-phase thickness squared. It also depends strongly upon the surface tension forces. The upper bound of time-to-fracture, when surface tension dominates,

and the lower bound, when surface tension forces are insignificant, are calculated and shown to differ by two orders of magnitude. By putting together the results from Publication IV and Publication V, we calculate a time-to-fracture for silicon-nitride (HS110) at an applied stress of 8×10^9 dynes cm^{-2} and at 900°C, of 0.18 to 46.5 hours. The wide range results from the two bounds discussed above. These numbers are in fair accord with real measurements on silicon-nitride (Evans and Wiederhorn, J. Mat. Sci., 9, 1974, p. 270).

3. PERSONNEL SUPPORTED ON AFOSR GRANT #74-2603

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Faculty

C. N. Ahlquist, Principal Investigator
20% time, 7 months A.Y.
100% time, 2 months Summer

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M. Forsha, Lab Assistant
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PERIOD II

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Student

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Technician

R. S. Twomey

[PII Redacted]

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5. PUBLICATIONS

Publications

I. C. N. Ahlquist, "The Influence of Yield Strength on Fracture of Semi-Brittle Ceramic Crystals," Acta Met. 22, (1974), p. 1133.

II. C. N. Ahlquist, "On the Interaction of Cleavage Cracks with Second Phase Particles," Acta Met. 23, (1975), p. 239.

III. C. N. Ahlquist, "Solution Strengthening of MgO," Proceedings of a Symposium on Deformation of Ceramic Materials, Penn State, July 17-19, 1974, Plenum Press. Jour. App. Phys. 46, (1975), p. 14.

IV. D. R. Mosher, R. Raj and R. Kossowsky, "Measurement of Viscosity of the Grain-Boundary Phase in Hot-Pressed Silicon-Nitride," submitted to Journal of Materials Science, May 1975.

V. R. Raj and C. H. Dang, "De-Adhesion by the Growth of Penny Shaped Voids in an Adhesive Layer," submitted to Philosophical Magazine, May 1975.

Papers Presented

1. Influence of Yield Strength on Fracture of Ceramics, Gulf Central Atomics, La Jolla, California, November 8, 1973.

2. Microstructural Effects During Fracture of Semi-Brittle Ceramic Crystals, Rockwell International Science Center, March 22, 1974.

3. Influence of Yield Strength on Fracture of Semi-Brittle Ceramic Crystals, AIME Spring Meeting, University of Pittsburg, Pittsburg, Pa., May 21, 1974.

4. Solution Strengthening of MgO, Symposium on Deformation of Ceramic Materials, Penn State, State College, Pa., July 17, 1974.

5. Publication IV, Spring AIME Meeting, Toronto, Canada, May 19-21, 1975.